Flexible Thermoelectric Power Generators Based on Electrochemical Deposition

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学位授与番号	工博第5437号
URL	http://hdl.handle.net/10097/00124757

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授　与　学　位	博士（工学）
学位授与年月日	平成３０年３月２７日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程） 機械システムデザイン工学専攻
学位論文題目	Flexible Thermoelectric Power Generators Based on Electrochemical Deposition（電気化学堆積に基づくフレキシブル熱電発電機）
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論 文 内 容 要 旨

Body area network (BAN) is a promising technology for many applications in the residential and medical fields. However, most of the wearable electronics devices based on this technology are still powered by batteries that need to be recharged and replaced frequently. For these wearable devices, it is necessary to have a power recharging mechanism without a user's interference. One possible solution for powering wearable devices without a battery is to harvest the thermal energy from human body temperature. The development of thermoelectric power generators (TEGs) has merited much attention due to its capability to convert low-grade waste heat into electrical energy using the Seebeck effect. However, human body are not flat but deformable, thus it indicates an essential need of flexible thermoelectric power generators **(**FTEGs) for the thermoelectric conversion applications. When a FTEG is attached onto the skin, the heat from the human body flows through the device. The voltage would be created in a FTEG due to the temperature difference between the skin and the ambient environment.

Electrochemical deposition is one of potential methods to synthesize thick films of thermoelectric materials with high quality morphology, compactness, thickness and thermoelectric properties. Using the electrochemically deposited materials for the applications of flexible micro devices has a great promise for thermal energy harvesters. However, due to the substantial obstacle of integrating the materials into flexible microsystem platform with controllable architectures, the application of electrochemical deposition is very limited to date. Therefore, this thesis mainly focuses on addressing the associated challenges by fabricating flexible thermoelectric power generators using electrochemical deposition method.

To fabricate and optimize the performance of FTEGs, there are many issues need to be solved. Because the temperature difference depends on the thickness of the thermocouples (TCs), using thicker thermocouples, the more heat energy can be harvested. However, the synthesis of thick thermoelectric materials in micro devices remains a challenge. In previous works, thermoelectric thin films of Bi_2Te_3 and Sb_2Te_3 have been deposited on solid or flexible substrates. In these studies, the thermoelectric energy conversion performances as an energy harvester are low due to the high internal electrical resistance of the thin film of thermoelectric elements. To enhance the working performances, thick films of thermoelectric materials are necessary. To achieve thick films of thermoelectric materials and improve the working performances, screen-printing, inkjet printing, molding, and vacuum deposition are the recently common methods. According to the previous works, all of best devices have been based on methods that allow synthesizing the thermocouples with the thickness of several hundred micrometers. Although the electrochemical deposition can synthesize thick films of thermoelectric materials, this method has not been effectively used for the applications on the flexible thermoelectric power generators so far. All of previous works based on the electrochemical deposition only aim to fabricate solid TEGs (STEGs). In this thesis, thick films of thermoelectric materials (Bi_2Te_3 and Sb_2Te_3) have been synthesized using electrochemical deposition for the fabrication of FTEGs. Moreover, enhancing the figure of merit *ZT* values of thermoelectric materials is also a difficult objective. So far, the figure of merit *ZT* values of thermoelectric materials at room temperature synthesized using electrochemical deposition are usually lower than other materials working at high temperatures.

Another obstacle that needs to be solved is the fabrication process. Because thermoelectric materials are electrochemically deposited on a solid silicon substrate. To fabricate a flexible device, a new fabrication process based on MEMS technology needs to be developed to integrate thermoelectric materials with a flexible support. Many previous works have reported that STEGs with electroplated materials can be completed by a two-substrate method. Herein, N-type and P-type thermoelectric materials are deposited separately on two different substrates. A single substrate with an individual material would be joined with each other at the end of the process. Another approach for STEGs fabrication is to deposit both N-type and P-type thermoelectric materials on the same substrate. The advantage of this method is that electrical contacts can be grown by the electroplating deposition or boding materials. However, this method encounters another problem. Since TCs are deposited on a metal seed layer, an electrical short-circuiting behavior in the TCs is caused if the seed layer is not removed. The laser cutting method has solved this behavior. Nevertheless, these methods can be only applied to solid membrane substrates. Hence, the fabrication of FTEGs based on sputtered or evaporated thermoelectric materials upon a flexible substrate is still a widely used method. That is the reason why all the best FTPGs to date are based on a print-screening method, which shows the possibility to synthesize thick thermoelectric films. However, the print-screening method has the disadvantage of the low integration of TCs.

Structures of the device can improve the temperature harvesting performance. Therefore, many structures of FTEGs have to be discussed. All structures are simulated using the finite element method. Meanwhile, the actual devices are fabricated and compared to prove the validity of the idea. The thermal harvesting capability has been evaluated along with internal electrical resistances, open-circuit voltages, and generated power densities near room temperature under a free convection condition.

By solving afore-mentioned challenges, this research aims at developing flexible thermoelectric power generators for thermal energy harvesting applications from many approaches as follows:

The possibility of a deposition of thick and stable thermoelectric films using electrochemical deposition method has been demonstrated in chapter 2. The electrolytes are used with a low concentration of cations and ions, resulting in a controlled low deposition rate. Therefore, the amorphous material is easily crystallized during the pulsed deposition. By this method, without the necessity of using non-aqueous additives and a soluble anode, highly oriented Bi_2Te_3 and Sb_2Te_3 thick films with a bulk-like structure are successfully synthesized with high Seebeck coefficients and low electrical resistivities. Several hundred-micrometers-thick Bi_2Te_3 and Sb_2Te_3 films are obtained. The Seebeck coefficients for the Bi_2Te_3 and Sb_2Te_3 films are -150 ± 20 and 170 ± 20 μV/K, respectively. Additionally, the electrical resistivity for the Bi_2Te_3 is 15 ± 5 μΩ·m and is 25 ± 5 μΩ·m for the Sb_2Te_3. Both of Bi_2Te_3 and Sb_2Te_3 exhibit low conductivities of approximately 1.4 ± 0.1 W/m·K and 1.5 ± 0.1 W/m·K, respectively. As a result, the figure of merit ZT values of Bi_2Te_3 and Sb_2Te_3 are 0.32 and 0.24, respectively.

An idea of improving thermoelectric properties by inclusions of nanoparticle in composite materials approached by the electrochemical co-deposition is demonstrated in chapter 3. The 5 nm-diameter gold particles are embedded in the nanostructure of Bi_2Te_3. As a result, the Seebeck coefficient is achieved as much as 2.5 times larger than the best result obtained in chapter 2 (~ -400 μV/K) while the electrical resistivity increases by the factor of seven (~140 μΩ·m). Additionally, the thermal conductivity of Bi_2Te_3 composite is approximately three times smaller than that of Bi_2Te_3 (~0.5 W/m·K and 1.4 W/m·K, respectively). Finally, the figure of merit *ZT* of composite material is approximately 0.62, which is two times larger than that of Bi_2Te_3 (~0.3). The gold nano-particles bismuth telluride shows the best values of Seebeck coefficient, thermal conductivity and figure of merit *ZT* among the bismuth telluride synthesized using the electrochemical deposition to date.

A new fabrication of flexible thermoelectric power generators approached from the electrochemical deposition method and MEMS technologies is introduced in chapter 4 and chapter 5. A new fabrication technique based on MEMS technology, using a silicon substrate as a sacrificial substrate is proposed and performed to realize self-supporting flexible micro-devices. With the proposed process, π-type and Y-type FTEGs have been successfully fabricated. Two π-type generators with different material combinations (Bi_2Te_3-Cu and Bi_2Te_3-Sb_2Te_3) are fabricated and compared in chapter 4. The devices are fabricated with the π-type structure embedded in a flexible material, where the top and bottom supporting substrates are eliminated. The thickness of Bi_2Te_3 and Sb_2Te_3 thermocouples is 200 µm. The usage of the thick thermoelectric films is especially advantageous for devices operating at small-to-moderate temperature differences, such as the human body temperature. From the human body temperature (~37ºC) and environment ambience (15°C), the Bi_2Te_3-Cu and Bi_2Te_3-Sb_2Te_3 based devices can harvest approximately from 2 ~ 4ºC temperature difference and generate high output power densities from 1 μW/ cm^2 and 4 $\mu W/cm^2$, respectively.

An idea of lateral Y-type TE cells instead of conventional vertical π-type cells is proposed to enhance the performance of harvesting the temperature in chapter 5. The advantages of the novel Y-type structure have been proved to optimize the device performance significantly. Basically, the structure consists of N type-bismuth telluride and P type-antimony telluride, which are deposited laterally on the membrane. The Y-type structure of TCs sandwiched between two thick polymer layers with low thermal conductivity can reduce the heat loss in the vertical direction. Heat is guided to the TCs via copper thermal guides, which are designed to lead the heat flux vertically from bottom to top sides of the device. A new fabrication process is also proposed for the Y-type structure. The larger temperature difference is obtained due to the longer-distance heat transfer of Y structure. With the temperature difference between the human body (approximately 37°C) and environment ambience (15°C), fabricated devices can harvest approximately 6ºC. The output power of the device is approximately 3 $\mu W/cm^2$.

In summary, this thesis has successfully fabricated FTEGs using the electrochemical deposition. The highly scalable and new devices demonstrated in this work open up opportunities for the applications of electrochemically deposited thermoelectric materials.

論文審査結果の要旨

人体などから生体情報を取得して無線ネットワークで情報を管理するためのボディーエリアネットワークに用いられる電源として，フレキシブルな熱電素子を利用することが期待されている。このためには，室温近傍で発電性能に優れた熱電材料を用いてフレキシブルな熱電素子を開発する必要がある。BiTe-SbTe 系の熱電材料は室温近傍で最も熱電性能が高い材料であるが，これまでに高い熱電発電性能を持ち，安価なプロセスで製造できる BiTe-SbTe 系のフレキシブルな発電素子は開発されていない。本研究は電解めっきを用いて高い熱電性能をもつ BiTe-SbTe 系の厚膜を堆積する技術を開発し，実際にフレキシブル熱電素子を試作してその発電性能を評価したものである。本論文は，これらの研究成果をまとめたものであり，全編 6 章からなる。

第 1 章は序論であり，本研究の背景や目的について述べている。

第 2 章では，厚膜の熱電材料である Bi_2Te_3 と Sb_2Te_3 を堆積する技術，およびその熱電特性の評価について述べている。電解めっきのめっき浴を最適化し，かつパルスめっき手法を用いることで，高い熱電性能を持ち，400-600μm の厚さの厚膜化が可能な堆積手法を見出している。Bi_2Te_3 と Sb_2Te_3 のゼーベック係数はそれぞれ-150μV/℃および 150μV/℃であり，高い値を示している。また，熱伝導率や電気抵抗率についても計測を行い，これらの厚膜が電解めっきで形成された膜としては高い性能指数を持つことを見出している。これらの結果は，フレキシブルな熱電素子を形成するための重要な成果である。

第 3 章では，更に熱電性能を高めるための手法として，電解めっきを用いた熱電膜と金微粒子の複合膜化について述べている。めっき浴に金微粒子を分散させることで，BiTe 膜中に金の微粒子を分散させることに成功している。この金微粒子の膜中分散により，ゼーベック係数が大きく熱伝導率は小さく，微粒子が分散していない試料と比較して性能指数を約 2 倍の 0.62 にできることを見出している。この成果は，電解めっきで形成する熱電材料の熱電性能を向上するための重要な知見である。

第 4 章では，π型の熱電発電構造をもつフレキシブル熱電素子について述べている。π型のフレキシブル熱電素子の構造を提案しその設計論について論じ，作製方法を開発している。実際に作製したフレキシブル熱電素子の性能を評価し，体温（37℃）と外界（16℃）の温度差により，4μW/cm^2 の発電ができることを示している。この成果は，フレキシブルな熱電素子を実現するための設計や製造にかかわる重要な成果である。

第 5 章では，熱電膜がある程度薄くても発電が可能な Y 型の熱電発電構造をもつフレキシブル熱電素子について述べている。Y 型のフレキシブル熱電素子の構造を提案しその設計論について論じている。実際に作製したフレキシブル熱電素子の性能を評価し，体温と外界（16℃）の温度差により，3μW/cm^2 の発電ができることを示している。この成果は，フレキシブルな熱電素子を実現するための設計や製造にかかわる重要な成果である。

第 6 章は結論である。

以上要するに本論文は，フレキシブル熱電変換デバイスに応用するため，電解めっき法により BiTe-SbTe 系厚膜の熱電性能向上に関して重要な成果を得て，実際にフレキシブル熱電素子を試作，評価して実証したものであり，機械システムデザイン工学，およびナノテクノロジーとマイクロシステムの融合による精密機械システム学の発展に寄与することが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。